

MECHANISTIC STUDIES OF CARBON DEPOSITION IN METHANE REDUCTION WITH IRON-BASED COMPOSITE PARTICLES

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Abstract

Chemical Looping Combustion (CLC) process has been widely considered to be clean energy conversion technology which utilizes an oxygen carrier to oxidize the fuel to H_2O and separated CO_2 efficiently. Therefore, the performance of the oxygen carrier (normally iron oxides) is critical to CLC. Although it has been found that the performances for reduction stage among these supported iron oxides are distinct from one to another, indicating complex iron oxide-support interaction, the understanding of these interactions including carbon deposition in methane reduction process remain limited, which could hamper the development of more efficient methane conversion system in CLC. Therefore, it is essential that a careful mechanistic study of methane reduction process be undertaken. In this study, efforts have been focused on understanding the mechanistic aspects of methane reduction process, among which carbon deposition and other key factors (such as supporting materials) to this process were carefully investigated. Iron oxides with three supporting materials, MgAl_2O_4 , MgO and Al_2O_3 , have been synthesized. Their combined reactivity, effect of supporting materials on the reaction, and corresponding reaction mechanisms have been studied using Thermogravimetric Analyzer (TGA), Brunauer-Emmett-Teller (BET), and Scanning Electron Microscope (SEM). It has been found that all three supported iron oxides, MgAl_2O_4 , MgO and Al_2O_3 , have the largest surface area and pore volume at point 4 (on TGA figure), where significant methane decomposition took place. The huge surface area and pore volume are believed to be largely attributed to the deposited carbon on solid samples. Correlations between the surface area (along with total pore volume) and the reaction pattern have been established by thoroughly analyzing results obtained from BET. During this stage of reduction, the MgO -supported iron oxides displayed the greatest reaction rate among all three synthesized particles. The reasons for the different behaviors may

be attributed to the crystal structure change in the particles and different reaction pathways involved during redox reactions. Reactive sites in iron oxides are critical to the redox reactions, and they are closely related to the morphology of porous surface for the particles. Therefore, SEM was used to directly observe the morphological change of surfaces of unreacted and reacted particles among the reaction cycles.

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1. Introduction

Inexpensive and plentiful energy resources are critical to sustain high living standard for human being. The discovery and exploration of shale gas has provided the U.S. with abundant energy resources because shale gas has been widely recognized as the next key domestic energy resource. Unfortunately, large quantity of CO₂ emission caused by methane combustion has increasingly raised environmental concerns. Therefore, it is necessary to develop efficient technologies that safely use fossil fuels with controllable carbon emission.¹ Chemical-Looping Combustion (CLC) process utilizes methane as feedstock and metal oxides as oxygen-carriers (OC) to deliver oxygen from air to methane, avoiding direct fuel combustion with air. CLC produces sequestration-ready CO₂ stream, reducing the energy penalty of CO₂ separation from flue gases. The development of effective metal oxides thus becomes critical to the success for a CLC process. More importantly, the understanding of metal oxide involved reaction mechanism will help guiding future preparation of an applicable oxygen-carrier to successfully operate a CLC system. In particular, methane reductions by supported metal oxides will be carefully investigated in this research in order to obtain useful information to understand the mechanism.

1.1 Shale Gas - New Sources of Natural Gas (Methane)

Thanks to development of drilling technologies and increasing exploration efforts, shale gas is rapid increasing as a new source of natural gas in the United States. With the abundant amounts of natural gas discoveries from shale rocks, approximated reserves of US natural gas in 2008 were 35% higher than those in 2006.² The successful shale gas economy triggered the development of shale gas all over the world including North American, Europe and Asian countries. In the United States alone, the recoverable shale gas fields has been more than doubled from 353 trillion cubic feet to 827 trillion cubic feet based on the data of the US Energy

Information Administration (EIA) collected from the new shale gas fields located in Marcellus, Haynesville, and Eagle Ford shale.³ Other than as the next abundant domestic energy resource, the most important applications of shale gas are the preparation of nano-materials such as carbon nanotubes (CNTs) which has generated considerable excitement when initial reports were published showing high storage capacities for hydrogen, and the production of hydrogen.

1.2 The Syngas Chemical Looping (SCL)

The Syngas Chemical Looping (SCL) process, developed at the Ohio State University (OSU), converts gaseous fuels such as syngas (CO/H₂ derived from coal) or hydrocarbons into hydrogen while capturing 100% of CO₂ generated⁴. This can be achieved *via* a specially tailored iron-based composite particles, as a result, the hydrogen and electricity product cost is substantially reduced.^{5,6} The main reactions occurred in above process using natural gas (methane) and designated operating conditions are listed in Table 1.⁷

1.3 Oxygen Carriers and Reaction Mechanisms

A successful operation of chemical looping processes strongly depends on the effective performance of the looping particles (Figure1). The looping particle serves as an oxygen carrier and is commonly composed of metal oxides. One of the goals in oxygen carrier development is to optimize the efficiency of the release of oxygen from metal oxides during both reduction and oxidation reactions. The complete combustion of fossil fuels affords the reactor flue gases containing only CO₂ and H₂O, whereas partial combustion of fuels leads to the CO and H₂ products as well as possible carbon deposition onto solid oxygen carriers. The potential benefit of the increasing oxygen use at the metal oxide reaction site would be to increase the rate of conversion and to achieve a more complete combustion of the fuel in order to improve the

performance of the oxygen carrier. A patented iron-based composite oxygen carrier particle has been synthesized in order to prove the recyclability. The highly desirable properties of oxygen carrier include, a) good oxygen carrying capacity; b) high rates of reaction; c) satisfactory recyclability and durability; d) excellent mechanical strength; e) suitable heat capacity and high melting points for all oxidation states; f) resistance to contaminant and inhibition of carbon formations; g) low material cost; h) little environmental concerns. These important properties of oxygen carrier particles become indispensable elements for the success of further research on CLC process.

As one of preliminary studies on methane reduction with iron oxides, supported iron oxide at different reaction stages within a cycle are sampled and investigated by post-experimental solid characterization methods such as determining pore density by Brunauer-Emmett-Teller (BET, Figure 2) method. The largest surface area and pore volume were found to be where significant methane decomposition occurred, which are largely attributed to the carbon deposition on solid samples. The MgO-supported iron oxides perform distinctly from the other synthesized particles in terms of reduction behaviors. The reasons for the different behaviors may be attributed to the crystal structure change in the particles during methane reduction.

1.4 Gas-solid reaction theory

In most studies of the reduction and oxidation of metal oxides such as iron oxides, it is assumed that the gas – solid reaction is carried out in the following steps^{8,9}: 1) diffusion and/or convection of gaseous reactant across the gas stream to the surface of oxygen carrier particle, 2) diffusion of gaseous reactant through the pores of the particle, 3) adsorption of the gas reactants onto the reactive solid pore surface, 4) chemical reaction on the pore surface, 5) desorption of gaseous products from the pore surface, 6) diffusion of gaseous products out of the particle.

2. Methodology: Experimental Design

It is important to keep track of oxidation state of the metal/metal oxide throughout the reaction cycle in order to obtain useful information for studying the reaction mechanism. To do this, the experimental data has carefully collected from TGA with various solid-gas reaction conditions. Optimization of the reactions has been focused on the reduction step where carbon deposition was found to occur previously in the preliminary study. A series of experiments were designed to reach its optimal conditions including particle sizes, reaction temperatures and gas flow rate combinations, in order to get the maximum mass conversion of the oxygen carriers (iron oxide).

In addition, to obtain further information of the complex iron oxides-support relationship to help us understand the mechanism for the carbon deposition, the sampled supported iron oxides at different stages have been investigated by the post-experimental solid characterization methods: examining surface morphology by Scanning Electron Microscope (SEM) and determining the stage of carbon deposition by carbon analyzer. These results are believed to provide important information about the reduction mechanism in CLC with methane.

Experiment 1: TGA Experiment

A Setaram SETSYS Evolution Thermogravimetric analyzer (TGA) was used to study kinetics of the two-stage redox reaction cycle of iron oxides with three different kinds of support materials, magnesium oxide (MgO), aluminum oxide (Al_2O_3) and magnesium aluminate (MgAl_2O_4). The TGA was set up to operate at 900 °C for one cycle of redox reaction (1h reduction, 0.5h flush, 1h oxidation). The gas flow rate of CH_4/air , which is for reduction and oxidation, was set at 50

mL/min. The flow rate of N₂, the inert gas for flushing reaction mixture out of the reactor between reduction and oxidation, was set at 50 mL/min. In addition, the flow rate of helium, the protective gas for TGA, was set at 100 mL/min. The results are shown in the following figures (Figure 1.a, 1.b and 1.c).

Experiment 2: BET Experiment

Solid samples obtained from TGA experiment were tested in a NOVA 4200e analyzer (Quantachrome Co.). The surface area and pore volume were measured at -193 °C using liquid N₂ as adsorbent. Prior to absorption analysis, the sample was placed in the Degas vacuum system under ultra high vacuum at a temperature of 300 °C overnight. Nitrogen was back-filled and then the sample was transferred to the analysis system after it was cooled down. The sample was degassed again under ultra high vacuum at room temperature (20 °C) for a period of at least 8 h. Absorption analysis was experimented with liquid nitrogen as adsorbent at temperature of -193 °C. Surface area and total pore volume were calculated from N₂ adsorption data by multi-point BET analysis. Similarly, pore distributions were calculated from N₂ adsorption data by BJH pore distribution analysis.

Experiment 3: SEM Experiment

Solid samples obtained from TGA experiment were analyzed by SEM (Scanning Electron Microscope) and EDS (Energy-Dispersive X-ray Spectroscopy) in a Quanta-200 SEM.

Results and Discussion

Previous experiments performed in our lab have shown that the reduction of all supported iron oxide pellets adopted a similar two-stage reduction pattern. This two-stage pattern was revealed based on the TGA experiments for three different support materials, specifically magnesium oxide (MgO), aluminum oxide (Al_2O_3), and magnesium aluminate (MgAl_2O_4). The two stages involved 1) reduction reaction of iron oxide by methane (weight losing); 2) carbon

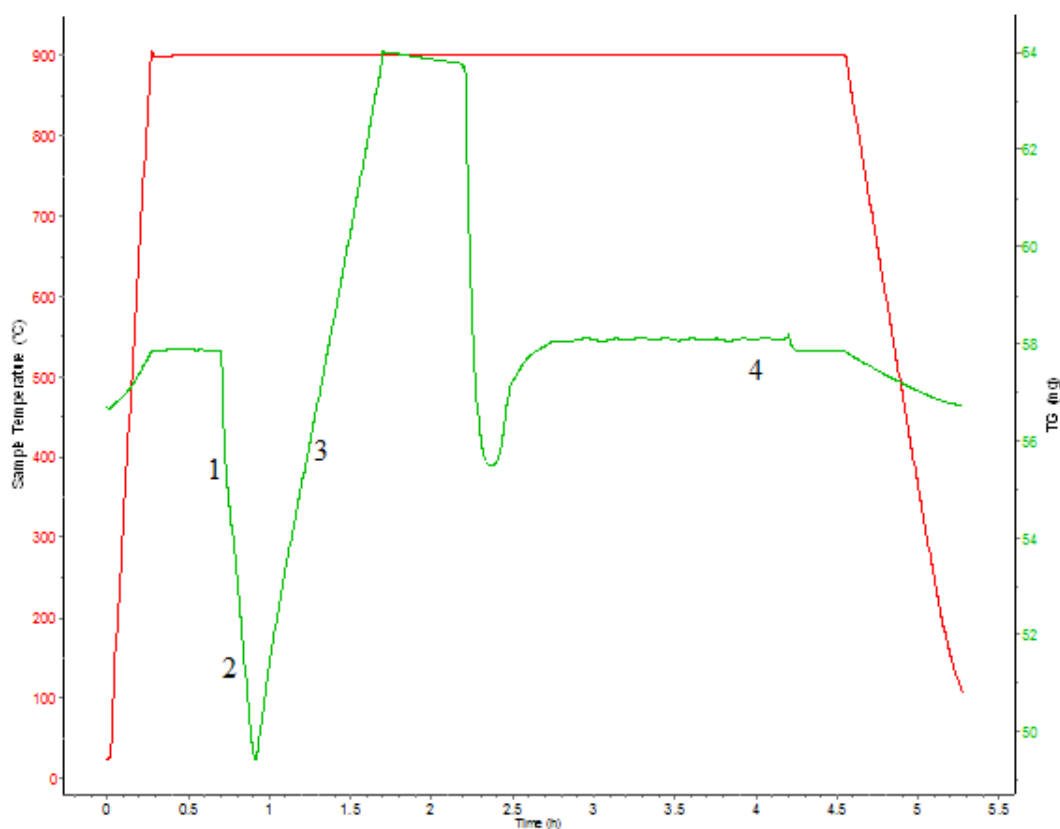


Figure 1.a. Two-stage Reduction of Fe_2O_3 with MgO as the support.

deposition from the decomposition of methane (weight gaining). The solid sample loses weight at the 1st stage as iron oxide is reduced, and the weights of the samples increase at the 2nd stage because carbon resulting from the methane decomposition is deposited on the surface of the samples without being further oxidized.

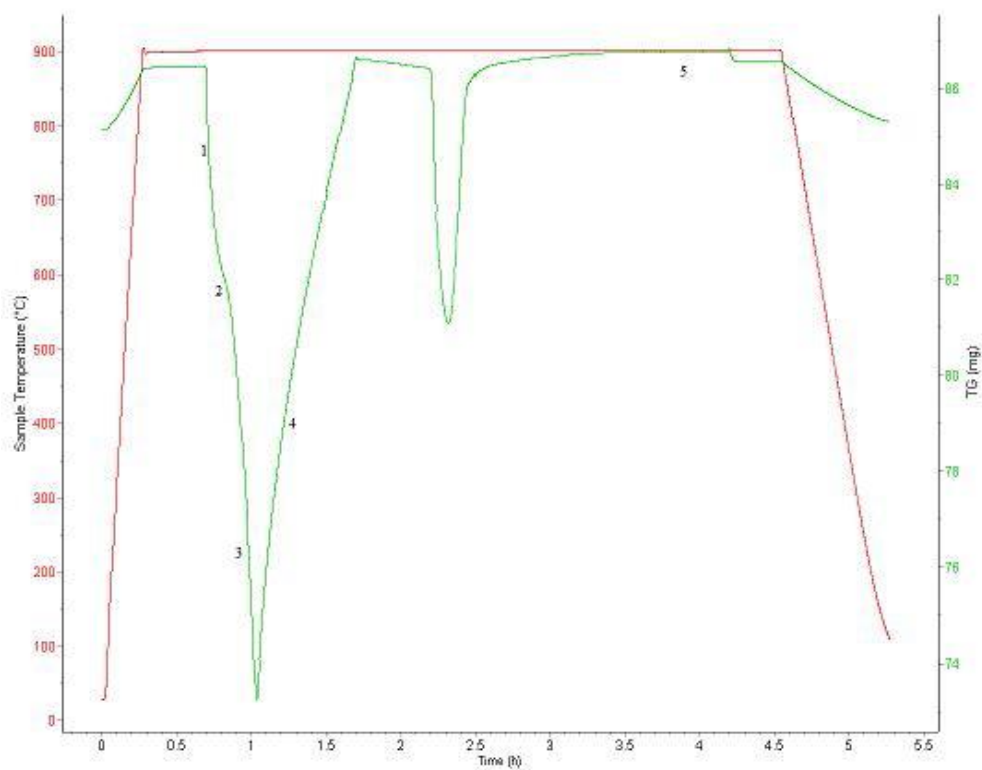


Figure 1.b. Two-stage Reduction of Fe_2O_3 with Al_2O_3 as the support.

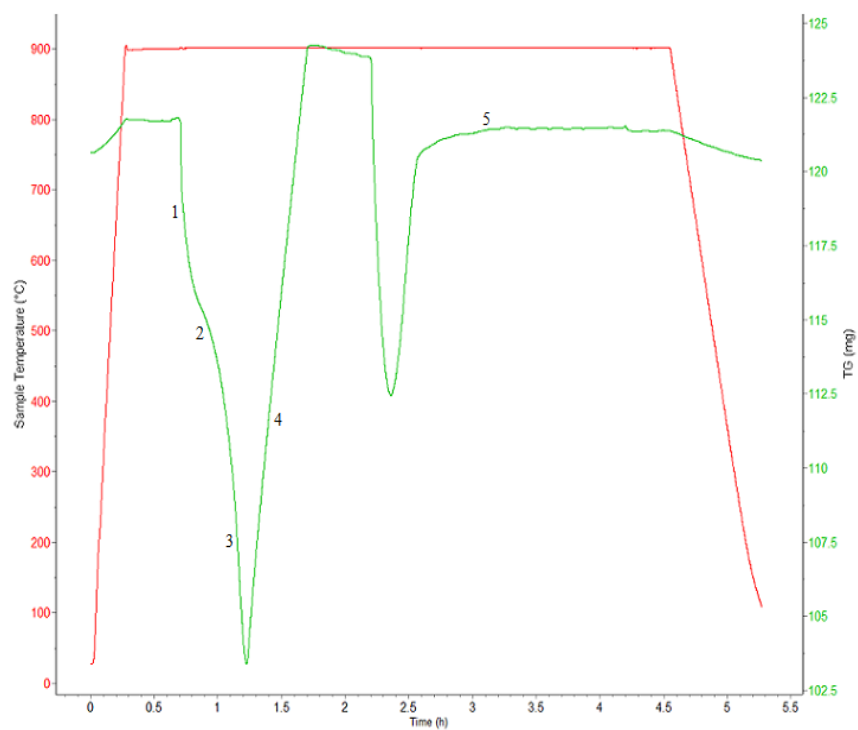


Figure 1.c. Two-stage Reduction of Fe_2O_3 with MgAl_2O_4 as the support.

Based on previous work in our research group, it has been proposed that the overall reaction rate, when using methane as the reductant at elevated temperature, is significantly affected by decomposition of methane leading to carbon deposition. And the carbon deposition occurred on the surface of the particle is believed to be responsible for the blockage of pores in the iron oxide particles, thus causing decreased reduction rate. The three different reaction rates can clearly be observed on above TGA figures obtained from iron oxide samples with three different supports based on different curve slopes during reduction process. Among these three oxygen carriers, the MgO-supported sample showed the fastest reduction rate as it gives the greatest slope. The decreasing order of curve slopes during reduction process is as the following $\text{MgO} > \text{Al}_2\text{O}_3 > \text{MgAl}_2\text{O}_4$. The Al_2O_3 -supported sample, however, displays a very similar pattern to that of the MgAl_2O_4 -supported sample with faster rate at the beginning and the end but slower rate in the middle. In principle, the redox chemical reaction is a process of electron transfer from one species (reductant, losing electrons) to another (oxidant, gaining electrons), and the degree of completion of the redox process is determined by electric potential of the reaction. This thermodynamic aspect of the reaction, however, is not necessarily associated with the reaction rate. The different reaction patterns may thus have to do with the different properties for the supporting materials. It has been noticed that their lattice energies have similar patterns to those of reduction reaction rate, that is, MgO bears much lower lattice energy than Al_2O_3 and MgAl_2O_4 , and the decreasing order. The decreasing order of lattice energy is as the following MgAl_2O_4 (19269 kJ/mol) > Al_2O_3 (15110 kJ/mol) >> MgO (3795 kJ/mol), implying that most stable supporting material (with the greatest lattice energy) mixing up with iron oxides gives the least rate whereas MgO (the least stable supporting particle with the lowest lattice energy) is able to afford the greatest reduction rate when mixing with iron oxide.

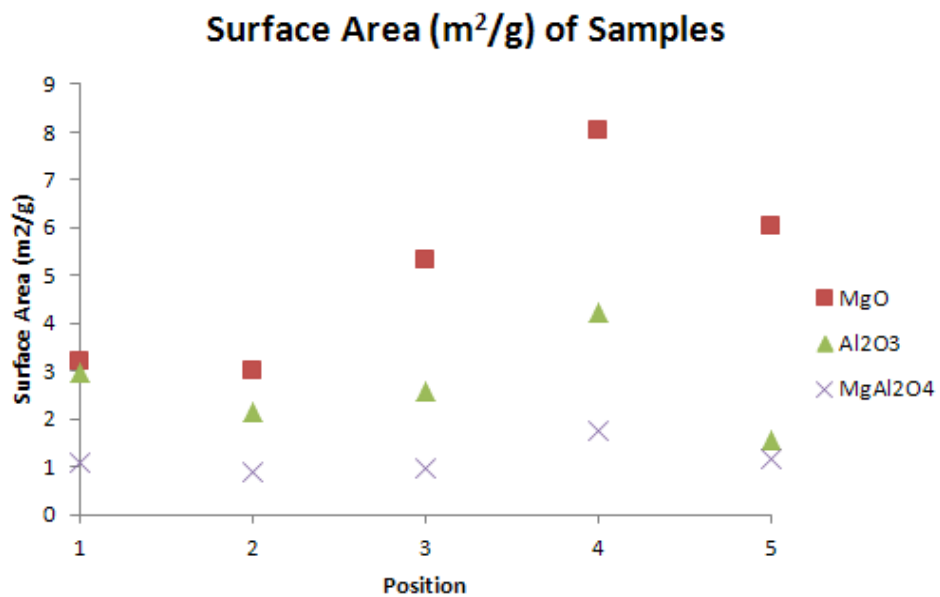


Figure 2. Surface area for supported iron oxide pellets at different stages (positions) within a cycle.

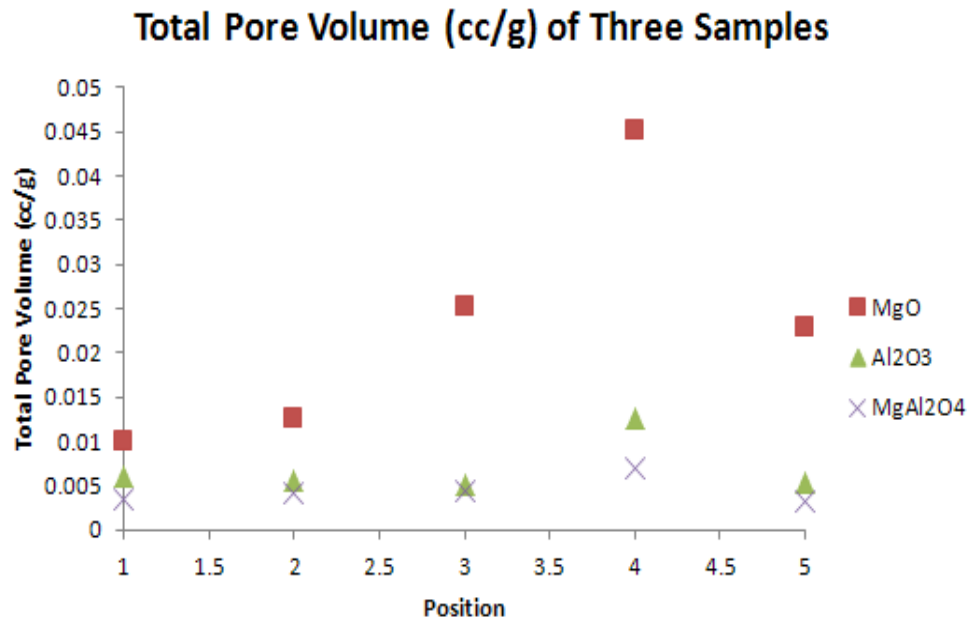


Figure 3. Total pore volume for supported iron oxide pellets at different stages (positions) within a cycle.

As shown in the results obtained from BET (Figure 2 and 3), both surface area and pore volume with MgO as the support gave much greater values than the other two, indicating MgO may be the best among three based on the following analysis. Greater pore volume implies better consumption of Fe_2O_3 , indicating Fe_2O_3 -MgO system to be the most reactive towards redox reactions. In principal, when one redox cycle is finished, both pore volume and surface area values should keep the same (supposing 100% conversion for all reactions). In the case of MgO, however, final pore volume is greater than the initial reading, indicating an incomplete oxidation process involved (more reduced form of Fe_2O_3 takes less room of the pore, thus leaving larger pore volume when the oxidation of Fe and/or FeO back to Fe_2O_3 is not complete). Under ideal conditions, since iron oxide experiences different stages of reactions, it is supposed to give different values for surface area and pore volume corresponding to different stages except for in the beginning (corresponding to position 1 in Figure #) and in the end (corresponding to position 5 in Figure #). All iron oxide supported with 3 different materials reach the maximum values of surface area and pore volume at the same position 4, indicating this is the stage when carbon deposition started and reached the peak value. In other words, the increase of surface area is caused by carbon deposition while pore volume reaching its peak value at this point indicates the completion of reduction.

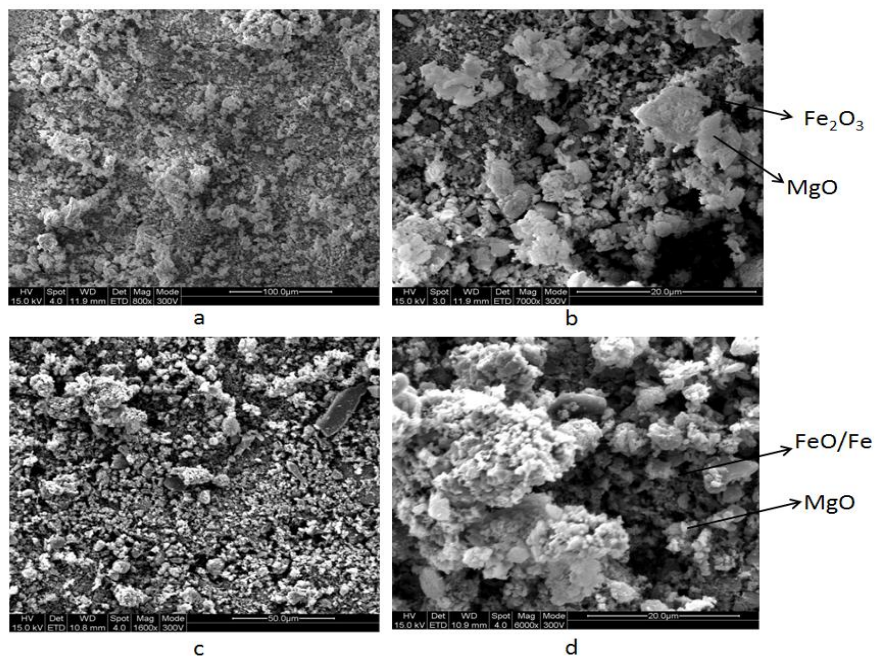


Figure 4. (a) (b) Unreacted $\text{Fe}_2\text{O}_3/\text{MgO}$; (c) (d) Reacted $\text{Fe}_2\text{O}_3/\text{MgO}$ (P4)

In order to directly observe and compare the topography and composition of surfaces of fresh and reacted particles, samples were analyzed with Scanning Electron Microscope (SEM) and Energy Dispersive X-ray Spectroscopy (EDS) in a quanta-200 SEM.

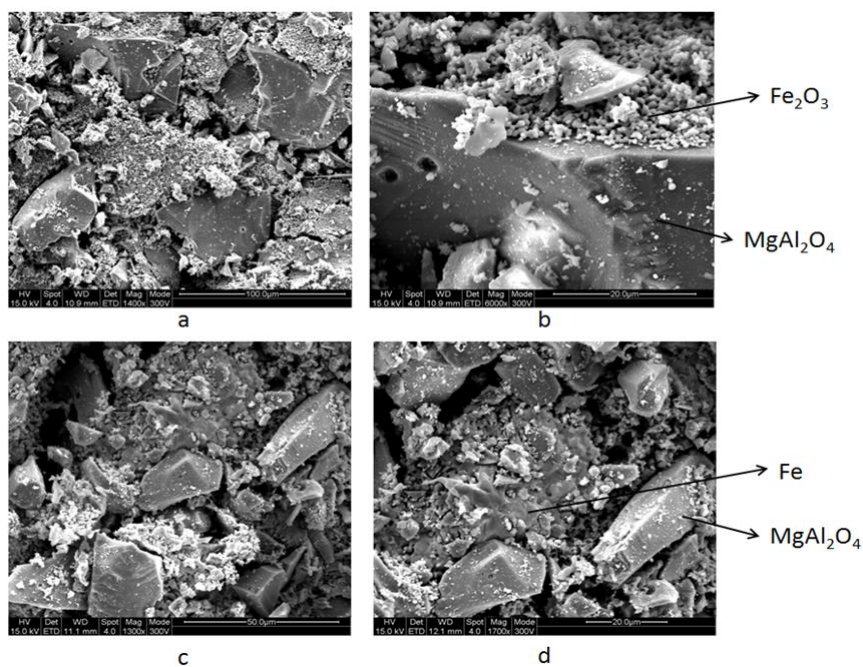


Figure 5. (a) (b) Unreacted $\text{Fe}_2\text{O}_3/\text{MgAl}_2\text{O}_4$; (c) (d) Reacted $\text{Fe}_2\text{O}_3/\text{MgAl}_2\text{O}_4$ (P4)

Different support materials have distinct changes in surface structures (Figure 4 and 5). For instance, $\text{Fe}_2\text{O}_3/\text{MgO}$ pellet was very porous after reaction (Figure 4), and this was consistent with the huge increase in surface area and pore volume as obtained from BET measurements. On the other hand, $\text{Fe}_2\text{O}_3/\text{MgAl}_2\text{O}_4$ pellet has typical spinel grain, and there is no obvious change in the spinel grain structure (Figure 5) although, metallic iron was also sintered. However, metallic iron dispersed among spinel grains rather than sintered into a large piece as in $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$.

7. References:

1. Miller, D. D., Siriwardane, R. "Mechanism of Methane Chemical Looping Combustion with Hematite Promoted with CeO₂", *Energy&Fuels*, **27**: 4087 – 4096. (2013).
2. J.Mouawad, "Estimate places natural gas reserves 35% higher", *New York Times*, 17 June 2009, accessed 25 March 2012.
3. "Annual Energy Outlook 2012 Early Release Overview". Retrieved 27 March 2012.
4. Energy Information Administration (EIA), Emissions of Green House Gases in the United States. DOE/EIA-0573 (2005).
5. McGlashan, N. R. "Chemical looping combustion – a thermodynamic study", *Proc. IMechE, Part C: J. Mech. Eng. Sci.* **222**: 1005 – 1019 (2008).
6. Brandvoll, O. and Bolland O. "Inherent CO₂ capture using chemical looping combustion in a natural gas fired cycle". *Trans. ASME* **126**: 316 – 321 (2004).
7. Fan, L-S. "Chemical Looping Systems for Fossil Energy Conversions", Wiley, A John Wiley & Sons, Inc. (2010).
8. E.T. Turkdogan, J.V. Vinters, *Metall. Trans.*, 11(1971)3189.
9. E.T. Turkdogan, J.V. Vinters., *Metall. Trans.*, 3(1972)1561.
10. B.B.L. Seth, H.U. Ross. *Transactions of the American Institute of Mining, Metallurgical and Petroleum Engineers*. 233(1965)180.